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<p>(21) International Application Number: PCT/EP96/04986 (22) International Filing Date: 14 November 1996 (14.11.96) (30) Priority Data: 195 44 293.8 28 November 1995 (28.11.95) DE (71) Applicant: DEGUSSA AKTIENGESELLSCHAFT [DE/DE]; Weissfrauenstrasse 9, D-60311 Frankfurt (DE). (72) Inventors: SCHÜTTE, Rüdiger, Im Goldenen Ring 11, D- 63755 Alzenau (DE). BEWERSDORF, Martin; Kasseler Strasse 22, D-63571 Gelnhausen (DE). KLASSEN, Claas- Jürgen; Am Silberberg 19c, D-63579 Freigericht (DE).</p>		<p>(81) Designated States: CA, CN, CZ, HU, IL, JP, KR, MX, NO, PL, RU, SI, SK, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i></p>
<p>(54) Title: COATED SODIUM PERCARBONATE PARTICLES, PROCESS FOR THE PRODUCTION THEREOF AND USE THEREOF (57) Abstract <p>In order to increase active oxygen stability, sodium percarbonate is coated with single or multiple layers of various substances. Sodium percarbonate particles coated according to the invention consist of a core of sodium percarbonate fluidised bed spray granulate and sodium sulphate, which may be partially hydrated, as the sole constituent of a single coating layer. The particles according to the invention exhibit both elevated active oxygen stability and very good ensilability. The coating layer is applied by spraying an aqueous Na₂SO₄ solution onto the particles to be coated, which were themselves produced by fluidised bed spray granulation, in a fluidised bed and vaporising water at a fluidised bed temperature of 35 to 100 °C.</p></p>		

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Coated sodium percarbonate particles, process for the
production thereof and use thereof

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Description

This invention relates to sodium percarbonate particles
having a single-layer coating comprising a core
10 substantially consisting of sodium percarbonate and a
coating layer enclosing the core and firmly adhering
thereto. Despite the use of a single coating material,
the coated sodium percarbonate particles are
distinguished by very good storage and ensiling
15 properties. The invention moreover relates to the use of
the coated sodium percarbonate particles in detergents,
cleaning agents and bleaches.

Sodium percarbonate ($2 \text{ Na}_2\text{CO}_3 \cdot 3 \text{ H}_2\text{O}_2$) is used as an
20 active oxygen component in detergents, bleaches and
cleaning agents. Due to the unsatisfactory storage
stability of the sodium percarbonate in warm/moist
surroundings and in the presence of certain detergent and
cleaning agent components, sodium percarbonate must be
25 stabilised against the loss of active oxygen (Oa). An
essential principle of stabilisation involves enclosing
the sodium percarbonate particles in a coating of
components having a stabilising action.

30 GB patent 174 891 teaches the stabilisation of compounds
decomposable by the action of weather or catalysts by

coating. Coating is achieved by spraying a coating component in liquid form onto the pulverulent material to be stabilised, which is maintained in motion; in order to avoid liquefaction or caking, the material is cooled or dried by means of a stream of air. Per compounds, such as sodium percarbonate, may be coated with water glass using this process. In the case of sodium percarbonate, it is not possible to achieve adequate stabilisation with a layer of water glass alone. In connection with coating soda containing water of crystallisation, this document also mentions Glauber's salt, namely sodium sulphate decahydrate, as a possible coating component. This document does not make it obvious to coat sodium percarbonate with a layer substantially consisting of sodium sulphate, which is not present in the form of the hydrates thereof or only partially so.

DE-OS 24 17 572 discloses a coated sodium percarbonate, wherein the coating substance is a mixed compound formed by crystallisation of sodium carbonate or bicarbonate with sodium sulphate. According to DE patent 26 22 610, apart from sodium sulphate and sodium carbonate, the single-layer coating additionally contains a sodium silicate. In both processes described in the above-stated documents, an aqueous solution of the constituents of the coating material is sprayed onto sodium percarbonate particles in a fluidised bed, while maintaining a fluidised bed temperature of between 30 and 80 °C, wherein a solid coating is formed by vaporisation of the introduced water. Despite distinctly improved stability of the sodium percarbonate particles coated in this

manner, the active oxygen content still decreases excessively in the event of extended storage in the presence of a detergent powder. It has additionally been found that coated sodium percarbonate particles having a coating, the outermost layer of which consists of soda alone or as the main component of a mixture, exhibit unsatisfactory ensilability in that beds of such products consolidate over extended periods of storage and thus exhibit poor flow behaviour and make handling more difficult.

By way of comparison, sodium percarbonate was also coated with soda alone and with sodium sulphate alone using the process of DE-OS 24 17 572. According to Table IV of this document, the resultant coated products exhibit substantially lower stability in moist/warm storage than products which contain in the coating both sodium sulphate and sodium carbonate in the form of a mixed compound. Even though DE-OS 24 17 572 does not state how the sodium percarbonate to be coated was produced, it may be assumed that the sodium percarbonate was obtained by a crystallisation process known at the filing date as production by fluidised bed spray granulation only subsequently became known.

According to DE-OS 43 15 380, the coating material of a coated sodium percarbonate consists of a mineral salt mixture substantially consisting of alkali metal sulphate and alkali metal chloride. Although such coated products exhibit satisfactory active oxygen stability and, provided that no alkali metal silicate is additionally

present, also an elevated dissolution rate, they are considered disadvantageous due to their content of alkali metal chloride and the associated corrosion hazard. There is no indication in this document of using sodium sulphate as the sole coating material.

According to US patent 4,325,933, the hygroscopic nature of sodium percarbonate may be reduced and stability increased with a coating of magnesium salts, in particular magnesium sulphate. However, a coating containing solely magnesium salts no longer fulfils current requirements for active oxygen stability. WO 95/02555 and EP-A 0 623 553 accordingly relate to coated sodium percarbonate particles, the coating of which additionally contains, apart from magnesium sulphate and a silicate, soda or an alkali metal salt from the range of carbonates, bicarbonates and sulphates. While a single- or multi-layer coating does indeed give rise to very good active oxygen stability, the necessity of using three different coating components is disadvantageous. Moreover, products having a multi-layer structure and soda in the outermost coating layer have a tendency to cake.

WO 95/15291 discloses a process for the production of sodium percarbonate particles having improved stability. In this process, sodium percarbonate is brought into contact with a gas having an elevated CO₂ content and moisture, in order to form a continuous sodium bicarbonate layer on the sodium percarbonate particles. A layer of sodium sulphate may additionally be applied onto

the sodium bicarbonate layer. The process is performed in a fluidised bed coating apparatus.

The object of the present invention is to provide further
5 coated sodium percarbonate particles which, despite having only a single coating component, exhibit very good active oxygen stability in detergents, bleaches and cleaning agents together with good ensilability.

10 This object is achieved by coated sodium percarbonate particles comprising a core substantially consisting of sodium percarbonate and a coating layer enclosing this core and firmly adhering thereto substantially consisting
15 of sodium sulphate, which may be partially hydrated, which particles are characterised in that the core consists of sodium percarbonate produced by fluidised bed spray granulation and the coating layer is obtainable by spraying an aqueous sodium sulphate solution onto the uncoated particles of the sodium percarbonate fluidised
20 bed spray granulate located in the fluidised bed and by evaporating water while maintaining a fluidised bed temperature of 35 to 100 °C.

The remaining claims relate to preferred embodiments of
25 the coated sodium percarbonate particles and to a process for the production thereof and to the use thereof.

The core of the coated sodium percarbonate particles substantially consists of sodium percarbonate, which has
30 been produced by fluidised bed spray granulation, wherein a hydrogen peroxide solution and a soda solution are

sprayed in a fluidised bed apparatus onto nuclei of sodium percarbonate or of other organic or inorganic substances and water is simultaneously vaporised. With regard to the production of the core substantially

5 consisting of sodium percarbonate by fluidised bed spray granulation processes, reference is made by way of example to DE-OS 27 33 935 and to WO 95/06615. The term "substantially" is taken to mean that, as a result of the production process, the core may contain small quantities

10 of auxiliary substances, i.e. substances other than sodium percarbonate. The auxiliary substances are conventionally present in a quantity of less than 20 wt.% and in particular of less than 10 wt.%, relative to the core. The auxiliary substances are in particular active

15 oxygen stabilisers, such as for example silicates and/or magnesium compounds. Another class of auxiliary substances comprises inorganic or organic compounds which are used as nuclei in fluidised bed spray granulation for the production of sodium percarbonate, for example soda

20 and other substances as are already used in conventional detergents and cleaning agents.

According to the invention, the coating layer substantially consists of sodium sulphate, which may be

25 partially hydrated.

The coating layer is preferably produced by means of a fluidised bed spray granulation process.

30 As is known, sodium sulphate forms various hydrates, in particular the decahydrate. So that a good stabilising

action may be achieved, endeavours are made during production to obtain a product having the lowest possible degree of hydration. For this reason, the fluidised bed temperature during application of the coating layer is maintained above the transition temperature of the decahydrate (32.4 °C).

The weight of the single-layer coating on the core substantially consisting of sodium percarbonate is usually between 0.5 and 25 wt.%, calculated without hydrate, relative to the sodium percarbonate. The entire quantity of coating preferably amounts to 1 to 15 wt.%, in particular 2 to 10 wt.%, in each case calculated without hydrate and relative to sodium percarbonate.

An essential feature of the coated sodium percarbonate particles according to the invention is that the coating layer is obtainable by the process according to the claims. As is clear from the Examples and Comparative Examples, selection of the material(s) in the outermost layer of the coating has a substantial influence on active oxygen stability and caking behaviour and consequently on ensilability.

As disclosed by DE-OS 24 17 572, sodium sulphate has not hitherto been taken into consideration as a sufficiently effective sole coating component for sodium percarbonate. When developing sodium percarbonate having improved active oxygen stability, it was considered necessary to use sodium sulphate in the form of mixed salts or as a constituent of a multi-substance composition. It was thus

surprising that very good active oxygen stability accompanied by excellent ensilability may be achieved by using a core of sodium percarbonate fluidised bed spray granulate and sodium sulphate as the sole constituent of the coating layer. While, for example, coated sodium percarbonate particles having soda in the outermost layer of the coating tend to cake during storage, this caking may be avoided if the outermost layer of the coating consists of sodium sulphate, which may be partially hydrated. Thanks to the good ensilability of the sodium percarbonate particles according to the invention, there is no agglomeration and thus no disruption of emptying nor arching in the silos, nor handling or dispensing problems with large and small containers.

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As already mentioned, the sodium percarbonate particles coated according to the invention may be produced by coating in the fluidised bed. The process for applying a coating onto sodium percarbonate by spraying an aqueous solution containing a coating component on uncoated sodium percarbonate particles located in a fluidised bed is known *per se*, reference is made by way of example to EP-A 0 623 553, WO 95/02555, US 4,325,933 and DE-PS 26 22 610, in which the process for fluidised bed coating is thoroughly described, but the sole use of sodium sulphate to produce an outermost coating layer is neither disclosed nor rendered obvious. A fluidised bed is formed using air as the fluidisation and drying gas and uncoated sodium percarbonate according to the invention. The Na_2SO_4 solution to be sprayed preferably has a sodium sulphate content of between 10 and 30 wt.%. This solution

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is sprayed by means of one or more spray nozzles onto the particles in the fluidised bed. Spraying preferably proceeds at a fluidised bed temperature of 50 to 80 °C. The air used for fluidisation and drying conventionally has a temperature of between 50 and 200 °C, in particular from 80 to 120 °C. The coating layer may be applied in conventional apparatuses for fluidised bed spray granulation, for example in substantially round fluidised bed apparatuses or in a flow channel. During or after application of the outermost layer of the coating, the material located in the fluidised bed or discharged therefrom may be subjected to a conventional classification process. The average grain diameter and the grain size range of the particles to be coated is selected in such a manner that the coated product according to the invention satisfies applicational requirements (a coarse material is often preferred with regard to elevated Oa stability, while a finer material is preferred with regard to a short dissolution time).

20

The sodium percarbonate particles coated according to the invention may be used as a bleaching component in detergents, cleaning agents, bleaches and disinfectants. In addition to conventional cleansers and scouring agents, the stated cleaning agents also include dishwashing detergents and denture cleansers. Such detergent, cleaning agent, bleach and disinfectant compositions are distinguished by the fact that the coated sodium percarbonate contained therein has unexpectedly high storage stability in the presence of conventional constituents, such as in particular

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zeolites, such that only very slow loss of active oxygen occurs during conventional storage of such compositions. The detergents, cleaning agents, bleaches and disinfectants consist of 1 to 99 wt.% of the sodium percarbonate particles coated according to the invention or of a mixture of these and other active oxygen bleaches and, for the remainder to 100 wt.%, of other conventional components of such agents. These components in particular include:

10

1. surface-active agents from the range of cationic, anionic, nonionic, amphoteric or ampholytic surface-active agents.

15

2. inorganic and/or organic builders, the principle action of which is to sequester or complex the metal ions responsible for water hardness, for example zeolites, phyllosilicates, polyphosphates, aminopolyacetic acids and aminopolyphosphonic acids as well as polyoxycarboxylic acids.

20

3. components having an alkaline action, such as alkanolamines, and inorganic electrolytes, such as silicates, carbonates and sulphates.

25

4. bleaching activators from the series of N-acyl compounds and O-acyl compounds, such as tetraacetythylenediamine (TAED) and nonanoyloxybenzene sulphonate (NOBS).

30

5. further constituents of the agents may be, stabilisers for peroxides, such as in particular magnesium salts, anti-redeposition agents, optical brighteners, foam inhibitors, enzymes, disinfectants, corrosion inhibitors, fragrances, dyes and agents to control pH. Reference is made by way of example to DE-OS 33 21 082, pages 14-30 with regard to individual compounds falling within classes 1 to 5.

Examples

- 5 a) General instructions for the application of a sodium sulphate coating on coated or uncoated sodium percarbonate in a fluidised bed:

10 A fluidised bed is created with the sodium percarbonate (NaPc) to be coated using drying air (air feed temperature 100 to 110 °C) in a laboratory fluidised bed dryer; the fluidised bed is maintained during coating. The particles present in the fluidised bed are sprayed with a 20 wt.% aqueous sodium sulphate solution, wherein the fluidised bed temperature is maintained in the range from 50 to 15 60 °C; post-drying is performed at 80 to 90 °C. The solution is sprayed using conventional two-fluid nozzles with air as the propellant. The quantities of coating stated in the Examples are weight percentages and relate in each case to the sodium 20 percarbonate used.

25 The single- or two-layer coated products not according to the invention were produced in a similar manner, wherein, however, one or two aqueous solutions containing coating components were sprayed onto the sodium percarbonate core.

- 30 b) Determination of storage stability of coated sodium percarbonate particles according to the invention and produced for comparison purposes in detergent formulations (= Oa retention (%)):

A phosphate-free detergent powder containing zeolite, activator TAED and a coated or uncoated sodium percarbonate (NaPc) are mixed together in quantities such that the mixture contains 5% TAED and the Oa content is approximately 2.35 wt.%.
5

Constituents of the detergent powder in wt.%:

	anionic surfactants	12
	nonionic surfactants	8
10	zeolite A	36
	soda	10
	Na silicates	3
	remainder (incl. moisture)	31.

800 g of each mixture are stored at 30 °C and 80% relative humidity in a conditioning cabinet in conventional commercial adhesively sealed E1 detergent packets having a water repellent coating. One packet is stored for each sampling time (after 4 and 8 weeks). Oa content is determined in the usual manner using the permanganate method; Oa retention in % is calculated from the starting Oa content and the Oa content after 4 and 8 weeks.
15
20

25 c) Determination of ensilability:

Ensilability was determined using the Jenike method (*Silo-Handbuch*, Peter Martens (ed.), Ernst & Sohn Verlag, Berlin (1988), pp. 41-56) over a period of 28 days. Product was stored largely with the exclusion of air at room temperature in sealed
30

measuring cells of the time consolidating bench.
 Tests were performed in the Jenike measurement cell
 (diameter: 92 mm) with a suspended weight $H = 251 \text{ g}$
 plus 1, 2 and 4 kg as the standard initial shear
 stress. For time consolidation purposes, product
 samples were exposed to an initial shear load of $H +$
 2 kg and final shear load of $H + 1 \text{ kg}$. Load during
 storage in the time consolidating bench 4.5 kg.

In the Jenike method, consolidation stress σ_1 [Pa]
 and bulk material strength f_c [Pa] are determined as
 a function of storage time. The ffc value is
 determined as a measure of the flowability of bulk
 materials using the equation:

$$ffc = \frac{\sigma_1}{f_c}$$

The results are rated as follows:

$ffc > 10$	free flowing
$ffc \text{ } 10-4$	ready flowing
$ffc \text{ } 4-2$	cohesive
$ffc < 2$	very cohesive, non-flowing.

The sodium carbonate coated was, on the one hand, that
 produced by fluidised bed spray granulation according to
 WO 95/06615 (see VB 1 in Table 1) and, on the other hand,
 conventional commercial sodium percarbonate produced by
 crystallisation from an aqueous solution containing NaCl
 (see VB 6 in Table 2).

Example B 1 and Comparative Examples VB 1 to VB 8

The products were produced in accordance with the general instructions. Table 1 shows the Oa contents. The total
5 moisture content of the coated products, determined by drying loss at 160 °C minus Oa content, was between 0.8 and 1.2%. Grain size range of the NaPc fluidised bed granulate: up to 0.5 mm 27%, up to 0.6 mm 40%, up to 0.7 mm 14%, up to 0.8 mm 16%, up to 1 mm 3%.

10

It may be seen from Table 1 that sodium percarbonate coated according to the invention with Na_2SO_4 as the sole coating (B 1) and two-layer coated NaPc with Na_2SO_4 as the outermost layer of a coating (VB 4) exhibit both
15 elevated Oa retention in the detergent formulation and good ensilability, namely "ready flowing" from the first day of storage; thereafter, there is no further change in flowability. Sodium percarbonate particles having an outermost layer substantially containing soda (VB 2 and
20 VB 3) consolidate during storage, they are classed as cohesive to very cohesive. It may be concluded from Example B 1 that a single-layer coating of an NaPc fluidised bed spray granulate with Na_2SO_4 gives rise to Oa retention which is substantially identical to that
25 achieved with a single-layer (VB 5) or two-layer (VB 4 and VB 3) coating containing Na_2SO_4 and Na_2CO_3 .

By way of comparison, Table 2 shows results for products not according to the invention, in which the core was in
30 all cases a crystallised NaPc. The active oxygen stability of an uncoated crystallised NaPc (VB 6) is

lower than that of an NaPC fluidised bed spray granulate (VB 1). While coating with Na_2SO_4 (VB 7 and VB 8) does indeed increase Oa retention in the detergent formulation and there is no tendency to cake, the Oa retention is
5 entirely inadequate for practical purposes.

Table 1

Example (B) no. or Comparative Example (VB) no.	NaPc core	NaPc coating (material/wt.%)	Oa content (%)	Oa retention (%) in detergent after 4 weeks and 8 weeks		Jenike ffc values as a function of storage time				
						Start	1 day	7 days	28 days	
VB 1	Fluidised bed spray granulate	-	14.2	52	25	n.d.	n.d.	n.d.	n.d.	
VB 2	"	Na ₂ CO ₃ / 5	13.5	56	34					
B 1	"	Na ₂ SO ₄ / 5	13.5	95	88	∞	7.9	7.9	7.9	
VB 3	"	1. Na ₂ SO ₄ / 2.5 2. Na ₂ CO ₃ / 2.5	13.6	92	89	∞	38	1.5	0.6	
VB 4	"	1. Na ₂ CO ₃ / 2.5 2. Na ₂ SO ₄ / 2.5	13.5	93	87	26.1	6.9	6.9	6.9	
VB 5	"	Mixture of Na ₂ CO ₃ and Na ₂ SO ₄ (1:1 parts by weight) / 5	13.6	95	86	n.d.	n.d.	n.d.	n.d.	

NaPc = sodium percarbonate; n.d. = not determined

Table 2

Example (B) no. or Comparative Example (VB)	NaPc core	NaPc coating (material/wt.%)	Oa retention (%) in detergent after 4 weeks	Tendency to cake *)
VB 6	Crystallised product	-	30	
VB 7	"	Na ₂ SO ₄ / 5	50	none
VB 8	"	Na ₂ SO ₄ / 10	70	none

*) qualitative rating: none - slight - moderate - severe (agglomeration when poured out of test flask after 10 days' storage in a sealed flask)

Patent claims

1. Coated sodium percarbonate particles comprising a
core substantially consisting of sodium percarbonate
5 and a coating layer enclosing this core and firmly
adhering thereto substantially consisting of sodium
sulphate, which may be partially hydrated, which
particles are characterised in that the core
consists of sodium percarbonate produced by
10 fluidised bed spray granulation and the coating
layer is obtainable by spraying an aqueous sodium
sulphate solution onto the uncoated particles of the
sodium percarbonate fluidised bed spray granulate
located in the fluidised bed and by evaporating
15 water while maintaining a fluidised bed temperature
of 35 to 100 °C.
2. Coated sodium percarbonate particles according to
claim 1,
20 characterised in that
the coating layer amounts to 0.5 to 25 wt.% of
sodium sulphate, calculated without hydrate and
relative to sodium percarbonate.
- 25 3. Coated sodium percarbonate particles according to
claim 2,
characterised in that
the coating layer amounts to 2 to 10 wt.% of sodium
sulphate, calculated without hydrate and relative to
30 sodium percarbonate.

4. Process for the production of coated sodium
percarbonate particles according to one of claims 1
to 3,
5 characterised in that
an aqueous sodium sulphate solution is sprayed onto
particles of the sodium percarbonate fluidised bed
granulate located in a fluidised bed while
maintaining a fluidised bed temperature of 35 to
10 100 °C and water is vaporised.
5. Process according to claim 4,
characterised in that
a 10 to 30 wt.% sodium sulphate solution is sprayed.
15
6. Process according to claim 4 or 5,
characterised in that
spraying is performed at a fluidised bed temperature
of 50 to 80 °C.
20
7. Use of the coated sodium percarbonate particles of
claims 1 to 3 as a bleaching component in
detergents, cleaning agents and bleaches, in
particular detergents and bleaches containing
25 silicate builders.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B15/10 C11D3/39 C11D3/08 C11D17/00

According to International Patent Classification (IPC) or in both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 24 17 572 A (INTEROX) 14 November 1974 cited in the application see page 2, paragraph 3 - page 3, paragraph 4 see page 4, paragraph 3 - page 5, paragraph 1 see tables 3,4	1,2,4,7
A	--- PATENT ABSTRACTS OF JAPAN vol. 018, no. 664 (C-1288), 15 December 1994 & JP 06 263434 A (TOKAI DENKA KOGYO KK), 20 September 1994, see abstract	1,4,7
A	--- EP 0 634 482 A (PROCTER & GAMBLE) 18 January 1995 see page 2, line 38 - page 3, line 10 --- -/-	1,2,4,7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 95 15291 A (KEMIRA OY ; KORVELA TIMO (FI)) 8 June 1995 cited in the application see page 1, line 4 - line 14 see table 1 ---	1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Appl. No.

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